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6. AUTHOR(S) Thomas M. Niemczyk				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Mexico Department of Chemistry Albuquerque, nm 87131			8. PERFORMING ORGANIZATION REPORT NUMBER 4	
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13. ABSTRACT (Maximum 200 words)  The aim of this project is to develop a technique that can be used to obtain information concerning the formation of chemical bonds, which relate to adhesion strength, at interfaces. The technique being developed is based on the application of a large electric field in the interface region of a multiplayer structure, and then using the field to Stark shift the infrared signals from the chemical bonds between the layers. Much of the work conducted over this report period was focused on improving the signal-to-noise ratio performance of the Stark shift infrared spectrometer. Significant noise sources were identified and a new "interleaved" operational mode of the spectrometer implemented that avoids the largest of the noise components. We also discuss the use of an epitaxially grown layer of silicon as an adhesion layer for structures consisting of a silica sol-gel film on a crystalline germanium substrate. The very thin silicon layer does not measurably affect the optical properties of these composite systems and solves the delamination problem that has limited the utility of these structures. We are now focusing on the application of the new infrared technique to polymer/metal systems and to the study of self-assembled monolayer systems with unique properties such as temperature driven phase transitions.				
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## REPORT DOCUMENTATION PAGE (SF298) (Continuation Sheet)

### Statement of Problem

The proposed project was directed at the study of interface structures, in particular at the characterization of adhesion forces at interfaces. There are numerous solid/solid interfaces where the adhesion of one component of the interface to the other is of critical importance. Examples include nonmetallic coatings or films on metal surfaces and reinforcement fibers in a variety of matrices. Thin films serve as corrosion barriers, lubrication layers, insulators, packaging materials, etc. The adhesion strength of these films, or coatings, to the substrate is critical to performance. When two solids join to form an interface an intermediate reaction region or mechanical interlocking region may be produced. The adhesion properties of an interface depend, therefore, on the morphological and chemical nature of the interface. A purely physical interaction, e.g. interlocking, depends on surface properties such as roughness. In many situations it is not desirable or practical to depend on a physical interaction as the basis of adhesion, hence the generation of chemical bonding is desired.

Testing for adhesion characteristics in an interface structure is generally mechanical, hence little information is produced concerning the nature of the chemical bonding at the interface that is responsible for the adhesion properties. A specific application that exemplifies the problem is the deposition of thin-layer low-k dielectrics in microelectronics manufacturing for insulating layers or packaging materials. Many of the leading candidates for the next generation of low-k dielectrics are fluoridated, or partially fluoridated, polymers. The formulations that produce the desired dielectric properties often lead to low adhesion strength which can lead to a potential delamination failure given the repeat thermal stresses encountered by many of these systems. Currently there is no good way to probe the molecular structure in the interface region of realistic systems.

We proposed the development of a technique capable of producing information that directly relates to chemical bond formation in interface structures. The instrument capable of providing these data will be assembled, characterized, and used to determine bonding in real interface samples. We envision this leading to a research program that studies adhesion in a variety of interface systems. Such a research program is multifaceted, hence the students involved will be forced to become familiar with a number of topics. The theoretical concepts involved in explaining adhesion, promoting adhesion in interface structures, producing interface structures, and participating in the characterization of the interface structures provides a fertile area for the training of research scientists.

The main theme of the proposed research plan was to construct and characterize an instrumentation system capable of collecting infrared spectral data, surface plasmon resonance data, and infrared Stark shift data from interface structures. The unique feature of the system proposed is a unique modulation scheme based on the Stark effect. The ability to selectively modulate the spectral features collected from the interface region allows discrimination from the much larger signals produced by the bulk materials. Thus, the goal of the project was to produce a well-characterized technique for the study of molecular bonding at interfaces.

## Summary of the most important results

**Instrument Design** A novel instrument system capable of collecting surface plasmon data, infrared reflection data, and Stark shift data from a sample was designed and constructed. A block diagram of this instrument is shown in Figure 1. Details of the instrument design are discussed more fully in Interim Progress Report No.1. This instrument system is unique, and capable of producing very useful information concerning the bonding at interfaces.

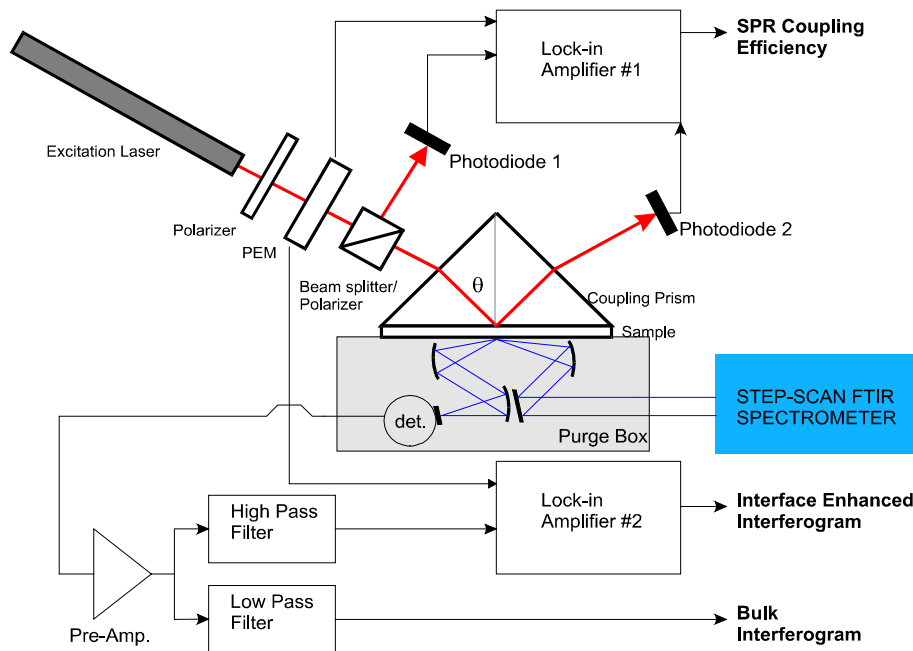


Figure 1. Block diagram of the SPR/FTIR/Stark-shift instrument.

**Instrument Performance Characterization** A considerable effort was made, after the instrumental system was fully assembled, to characterize the performance of the system. The signal-to-noise ratio (SNR) of the data produced in the infrared experiments was not as good as the models we had developed were predicting. The SNR of the experimental data is critical since exceedingly small signals are the target of the system. A number of minor improvements to the instrument were made before discovering that slow drifts in the infrared spectrometer were the fundamental limitation in the SNR. The experiment depends on recovery of signals that are the difference between two operational states. A solution to the long-term drift problems was found and implemented. We have termed this operational mode “interleaved” operation, for it allows for nearly simultaneous collection of the two operational states, hence eliminating drift problems, but can be carried out over long data collection periods necessary to recover the very small signals that are the target of the investigation. The implementation of the interleaved mode of operation was a critical development in this program, and is discussed more fully in Interim Progress Report No. 2. Results obtained using this interleaved mode of operation that demonstrate the gain in SNR are discussed in Interim Report No. 3.

Temperature Affects The Stark shift experiment depends on the ability to measure very small shifts in very small signals, hence sample and instrument stability are of utmost importance. An attempt was made using conventional temperature measurement techniques to determine if any heating occurred as a result of the laser interaction with the metal film. These attempts were not successful. We did, however discover a molecular approach to temperature determination based on conformational changes in a molecular system. The molecular system studied is one of a series of oligo(ethylene glycol) modified alkanethiols that will self-assemble into a monolayer on a gold surface. The conformational change leads to changes in the infrared spectra of the monolayer. The details of this system, and the infrared data collected as a function of temperature have been discussed in detail in Interim Progress Report No. 3.

Interface Adhesion Adhesion layers between layers are often used to promote system integrity. The adhesion of silica films to crystalline materials such as germanium and zinc selenide has been a problem, especially if the interface is to be exposed to a humid environment. We demonstrated that a solution to this problem was to coat the crystalline material with a very thin layer of epitaxial silicon, expose the silicon to air for a short period of time to promote the formation of a native oxide layer, and then overcoat that with the silica film. Interface structures created using this adhesion layer have proven very robust. Data collected from a germanium/silicon/silica structure are discussed in Interim Progress Report No. 3.

Although not a specific goal of the program originally described in the proposal to ARO, solving the delamination problem of sol-gel produced silica films deposited on crystalline germanium has allowed us to produce infrared sensors with unprecedented properties. We have coated a germanium waveguide with a sol-gel film, then surface modified the porous sol-gel to generate a film with the desired properties. These devices are capable of measuring infrared spectra from analytes in aqueous solution with sub parts-per-million detection limits. This represents about a three order of magnitude increase in sensitivity compared to anything previously appearing in the literature. A spectrum obtained from a 3.8 ppm solution of nitrobenzene using this sensor is shown in Figure 2.

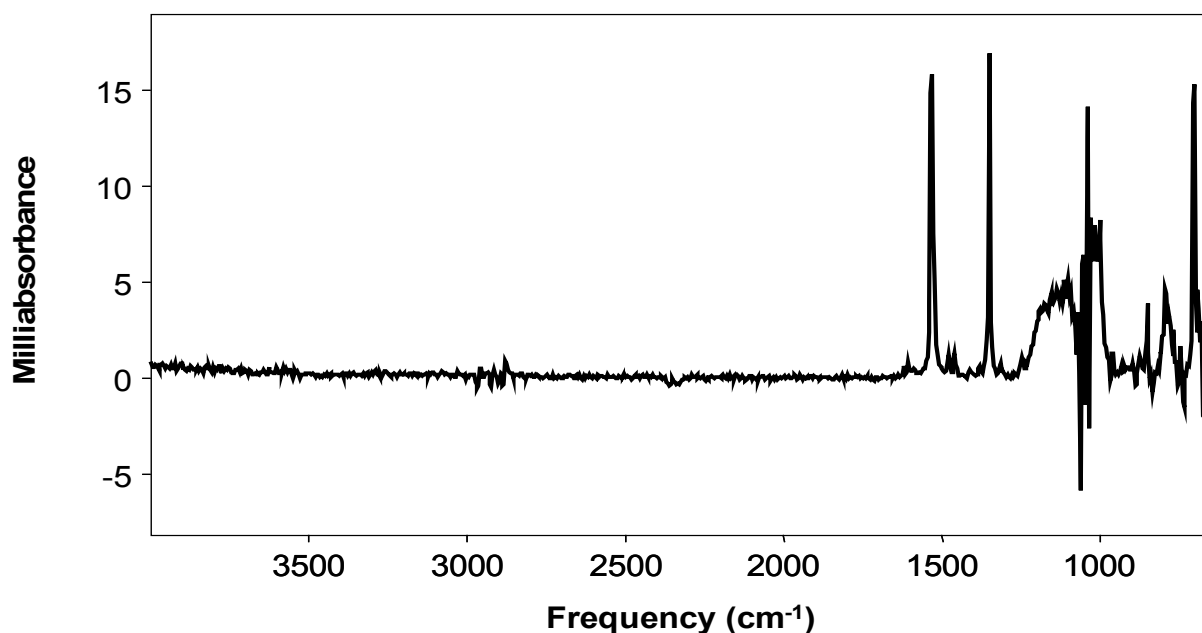


Figure 2. Spectrum obtained from a 3.8 ppm solution of nitrobenzene in water in contact with the surface modified sol-gel coated germanium waveguide.

Interface Spectra We have demonstrated that infrared and plasmon resonance data that can be used to show orientation and/or bonding can be collected from interesting interface structures. The orientation of monolayer phenol films deposited at metal surfaces as a function of deposition conditions has been studied. These studies were outlined in Interim Report No. 3. We have also completed a set of experiments demonstrating that we can fully characterized the formation of birefringent layers on a metal surface. In this study, we have investigated the adsorption behavior of phenol, (4-mercaptophenyl)-phthalimide (4-MPP), and (4-mercaptophenyl)-fluoro-phthalimide (4-MPFP) on gold and silver surfaces. The synthesis of the 4-MPP and 4-MPFP, deposition on gold surfaces, and preliminary spectra were discussed in Interim Report No. 3. Data have also been collected from polymer layers deposited on metal surfaces. In particular, the interaction between biphenylene dianhydride para-dianiline (BPDA) and aluminum has been studied. Although more work needs to be carried out on this system, we have been able to show that there are bonds that form due to the interaction of the C=O group and the aluminum surface. We have also studied the interaction of adhesion promoters. We have been able show infrared spectral features that are the result of bond formation between hexamethyldisilazane and gold, and have demonstrated that these signals can be recovered from a gold/hexamethyldisilazane/BPDA interface structure can be recovered. This latter experiment shows the high sensitivity of the instrumentation system developed here and how it can be used to study interface structures.

#### **Publications and Technical Reports**

##### **a. Papers Published**

“Extended Spectral Range Surface Modified Sol-Gel Coated Infrared Waveguides” Frederick G. Haibach, Arturo Sanchez, Jerrold A. Floro, Thomas M. Niemczyk, Applied Spectroscopy, **56**, 398 (2002).

##### **b. Conference Proceedings**

“Interface Specific RAIRS of Layered Solid Materials” MR Strunk, TM Niemczyk, and DM Haaland has been submitted for publication at PITTCO, March 12-17, New Orleans, LA.

“Interface Specific RAIRS of Layered Solid State Materials” Michael Strunk, Thomas M Niemczyk, and David M Haaland, PITCO 2000, March 12 - 17, 2000, New Orleans, LA

##### **c. Papers Presented at Meetings**

“Stark Modulation, Reflection/Absorption Infrared Spectroscopy of Interfaces”, Michael Strunk, Thomas M Niemczyk, and David M Haaland, FACSS 2000, September 24-28, 2000, Nashville, TN.

“Surface-Plasmon FTIR Investigation of a Phase Transition in Crystalline Self-Assembled Thiol Terminated Oligomers” Michael Strunk and Thomas M Niemczyk, FACSS 2001, Detroit MI, Oct. 7-12, 2001

“Extended Spectral Range Surface-Modified Sol-Gel Coated Infrared Waveguide Sensors” Frederick Haibach, Thomas M. Niemczyk, and Arturo Sanchez, FACSS 2001, Detroit MI, Oct. 7-12, 2001

##### **d. Manuscripts Submitted/in Preparation**

Drafts of papers with the following titles have been prepared:

“Surface-Plasmon FTIR Investigation of a Phase Transition in Crystalline Self-Assembled Thiol Terminated Oligomers”

“Formation and Characterization of Self-assembled Birefringent Mercaptophenyl-phthalimide Monolayers”

e. Technical Reports Submitted to ARO

Interim Progress Report No. 1 covering the period 21 Jun 99 to 31 Dec 99

Interim Progress Report No. 2 covering the period 1 Jan 00 to 31 Dec 00

Interim Progress Report No. 3 covering the period 1 Jan 01 to 31 Dec 01

**Participating Scientific Personnel**

Thomas M Niemczyk, Principal Investigator, assumed the position of Chair of the Department of Chemistry, June 2000.

Michael D. Strunk, Graduate Research Assistant (full time participant), has accepted a Postdoctoral Research Associate position in the Chemical Engineering Department at the University of South Carolina.

Frederick G. Haibach, Graduate Research Assistant (half time participant), PhD in May 2000, currently Postdoctoral Research Associate, Department of Chemistry, University of South Carolina.

Zachary Wilson, Undergraduate Research Student, BS in Chemistry May 2001, currently MD/PhD program at the University of Colorado in August 2001.

Arturo Sanchez, Undergraduate Research Student

Anding Zhang, Graduate Research Assistant (half time participant)

**Report of Inventions**

A patent disclosure (UNM-511) has been filed with the University of New Mexico patent office. Title: “Stark Effect Infrared Spectroscopy System”

Inventors: Thomas M Niemczyk, Michael R Strunk, Steven R Brueck

A disclosure entitled “Silicon Adhesion Layers” has been submitted to the UNM intellectual property office.

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SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

Thomas M. Niemczyk  
Department of Chemistry  
University of New Mexico  
Albuquerque, NM 87131